

Table of Contents

Time dependent quantum theory of reactive molecular collisions

Gabriel G. Balint-Kurti	1
1. Wavepacket propagation: Solving the time-dependent Schrödinger equation	1
2. Expansion of the propagator	2
3. Energy resolution and energy range of a wavepacket	3
4. Wavefunction and wavepacket	3
5. The hamiltonian	4
5.1 The overall hamiltonian	4
5.2 The radial kinetic energy terms: Radial grids and Fourier transforms	5
5.3 The angular kinetic energy terms	6
6. Preparation of the initial wavepacket	6
7. Analysis of product states: Calculation of the S-matrix	8
8. Reactant and product coordinate systems	8
9. Calculations for $J > 0$, centrifugal coupling and helicity decoupling ..	9
10. Angular basis functions and angular grids	10
11. Cross sections and reaction probabilities	11
12. J -shifting and capture models for estimating cross sections	11
13. Fourier transforms, absorbing the wavepacket at grid edge	12
14. New developments	13
14.1 Propagation of the real part of a wavepacket	14
14.2 Simplified propagation procedure	14
References	15

Quantum reactive scattering: the time - independent approach. I. Principles and early developments

Ralph Jaquet	17
1. Introduction	17
1.1 Remarks on quantum reactive scattering	18
1.2 Overview of quantum reactive methods and remarks on the coupled equations problem	21
2. Some aspects of quantum molecular scattering in chemical dynamics	25

2.1	Elastic Scattering	25
2.2	Inelastic Scattering	27
2.3	Reactive Scattering	30
3.	General remarks on quantum scattering	35
3.1	Evolution operator and Møller operators	35
3.2	Scattering Operator and scattering matrix	37
4.	Coordinate systems: collinear, planar, 3D, reduced degrees of freedom	38
4.1	Introduction	38
4.2	Jacobi coordinates	39
4.3	Hyperspherical coordinates	41
4.4	Natural coordinates	46
4.5	Coordinates used in the early H+H ₂ calculations	47
5.	Quantum reactive scattering in the nineteen seventies: H+H ₂ and the matching procedures	55
5.1	The quantum dynamics of collinear reactive triatomic systems	55
5.2	The quantum dynamics of three-dimensional reactive triatomic systems	65
5.3	Computational methodology	74
5.4	Results for H+H ₂	77
A.	Credits	78
	References	78

Quantum reactive scattering: the time - independent approach. II. Current methods and developments

Ralph Jaquet	83	
1.	Introduction	83
2.	Linear algebraic variational approach with Jacobi coordinates versus propagation methods with hyperspherical coordinates	83
2.1	Hulthén-Kohn variational principle	83
2.2	S-matrix version of the Hulthén-Kohn-variational principle	86
3.	The hyperspherical method	95
3.1	Introduction	95
3.2	Hyperradial equations	98
3.3	Asymptotic analysis	100
3.4	Computer implementation and applications	102
4.	Reduced dimensionality	102
5.	Recent developments	103
6.	Computer implementations and methodologies	104
6.1	Basis sets and grid techniques	104
6.2	Close coupling solvers	108
7.	Examples for “exact” calculations	111
7.1	Some remarks on Jacobi coordinates and scattering applications	111
7.2	H+H ₂	117
7.3	Other reactions	119

VIII Table of Contents

8. Summary 119
A. List of abbreviations 121
B. Credits 122
References 122

The Reaction Path Method for Chemical Reactions

Gert D. Billing 127

1. Introduction 127
2. Potential Energy Surfaces 128
 2.1 Preliminaries 128
 2.2 The Born-Oppenheimer separation 129
 2.3 Surface characteristics 131
3. The reaction path method 133
 3.1 Determination of the reaction path 133
 3.2 Reaction path constraints 135
4. Absolute rate-constants 137
5. Second quantization approach 141
 5.1 Formulation of the problem 141
 5.2 The transmission factor 146
 5.3 Initialization of the reaction path dynamics 148
6. Cross sections and rate constants 149
7. The reaction volume approach 151
 7.1 Reaction surface and reaction volume 151
 7.2 The kinetic energy 155
 7.3 The rotational coupling 157
 7.4 A simplified hamiltonian 161
8. Summary 162
A. Appendix A 163
B. Appendix B 165
References 166

Reaction rates

Uwe Manthe 167

1. Introduction 167
2. General theory 168
 2.1 Reactive scattering: state-selected and cumulative properties .. 168
 2.2 Rate constants in scattering theory 169
 2.3 Flux correlation functions 170
 2.4 Classical mechanics 172
 2.5 Transition state theory 173
 2.6 Quantum transition state theory 174
3. Quantum calculations 175
 3.1 Accurate evaluation of flux correlation functions 175
 3.2 The thermal flux operator 176

3.3	$N(E)$ -calculation	179
3.4	Rotational motion	181
4.	An approach to larger systems	183
4.1	The multi-configurational time-dependent Hartree approach ...	184
4.2	Statistical sampling	185
5.	Examples	187
5.1	The $\text{H}_2 + \text{OH} \rightarrow \text{H} + \text{H}_2\text{O}$ reaction	187
5.2	The $\text{H}_2 + \text{CN} \rightarrow \text{H} + \text{HCN}$ reaction	188
5.3	The $\text{O} + \text{HCl} \rightarrow \text{OH} + \text{Cl}$ reaction	188
5.4	The $\text{H}_2 + \text{Cl} \rightarrow \text{H} + \text{HCl}$ reaction	189
6.	Final remarks	190
	References	191



<http://www.springer.com/978-3-540-41487-2>

Methods in Reaction Dynamics
Proceedings of the Mariapfarr Workshop
Jakubetz, W. (Ed.)
2001, X, 195 p. 2 illus., Softcover
ISBN: 978-3-540-41487-2